

**COMPOSITION AND PROCESS FOR THE TREATMENT OF METAL  
SURFACES**

5

**FIELD OF THE INVENTION**

The present invention is directed to a composition and method for producing a conversion coating on metallic surfaces. The conversion coatings of this invention are generally chromium free and improve the corrosion resistance of the treated surfaces as well as the adhesion of siccative organic finishes to those treated surfaces. In addition, the conversion coatings of the present invention are minimally affected by subsequent heating and/or baking steps. This invention is particularly suited to treating zinc, zinc alloys, aluminum and aluminum alloys, although steel and other metals may be treated.

**BACKGROUND OF THE INVENTION**

Various conversion coatings for metal surfaces have been suggested in the prior art for the purpose of forming a coating, to protect the metal against corrosion and also serve as a base for improving the adhesion of subsequently applied siccative organic finishes. Such conversion coatings are created by treatment of the metal surface with solutions of various chemicals, which react with the surface to form the desired coating. Commonly used conversion coating compositions generally include phosphates and chromates.

Phosphate conversion coatings have long been used, particularly on steel. The simplest phosphating solutions comprise aqueous solutions of alkali metal phosphates that can react with iron, aluminum, and/or zinc to form the phosphate conversion coating. While phosphate conversion coatings do increase the corrosion resistance of the treated surface and the adhesion of subsequently applied siccative organic coatings, in many applications, better results are required.

Chromate conversion coatings generally produce much better corrosion resistance and adhesion than phosphate coatings. However, chromate conversion coatings generally do not provide good corrosion resistance and adhesion at elevated temperatures. Chromate solutions generally comprise aqueous solutions of hexavalent and/or trivalent chromium along with other additives. Historically, hexavalent

chromium has produced the best performing chromate conversion coatings. However, recent improvements in trivalent chromate technology have allowed trivalent chromates to rival the performance of hexavalent chromates. Typical chromate compositions and processes are revealed in U.S. Patent Nos. 5,407,749 and 4,349,392, the teachings of each of which are incorporated by reference herein in their entirety. In any case, chromium has been determined to be a relatively toxic metal and is heavily regulated. As a result, significant efforts have been expended to replace chromate coatings with chrome free coatings.

It is therefore an object of this invention to provide a composition and process which can produce a conversion coating on metallic surfaces, which coating will provide excellent corrosion resistance and adhesion to siccative organic coatings but is free of chromium content. In addition, it is an object of this invention to provide a conversion coating on metallic surfaces that is minimally affected by subsequent heating and/or baking. It is a further object of this invention to provide a composition and method for treating metal surfaces, especially the surfaces of zinc, zinc alloys, aluminum and aluminum alloys.

#### SUMMARY OF THE INVENTION

These and other objects of the present invention can be achieved by treating metal surfaces with a composition comprising:

- (1) a source of tungstate ions; and
- (2) a soluble material comprising zirconium; and thereafter drying or baking the metal surfaces.

The invention is particularly suited to the treatment of zinc and zinc alloy surfaces as well as surfaces of aluminum and aluminum alloys. The inventors have found that it is preferable to adjust the pH of the treatment composition to between 2.0 and 7.0. Preferably the treatment composition is free of chromium ions.

#### DETAILED DESCRIPTION OF THE INVENTION

The inventors herein propose a composition and process for the treatment of metal surfaces with a composition comprising:

- (1) a source of tungstate ions; and
- (2) a soluble material comprising zirconium; and thereafter drying or baking the metal surfaces.

5           The source of tungstate ions includes all tungstates but most specifically all ortho-tungstates, meta-tungstates and para-tungstates, polytungstates, hetero-polytungstates, isopolytungstates, peroxytungstates, and combinations thereof. A source of meta- or para-tungstate is preferred. Suitable sources of tungstate ions include sodium, potassium, lithium, calcium, cerium, barium, magnesium, strontium, hydrogen  
 10 and ammonium tungstate salts. ammonium metatungstate, potassium metatungstate, sodium metatungstate, tungstic acid, sodium tungstate, potassium tungstate and ammonium tungstate. A soluble tungstate salt, such as ammonium or potassium tungstate, is most preferred for use in both the liquid concentrate and in the treatment solution. The concentration of tungstate (measured as tungsten) in the composition  
 15 should range from about 0.01 g/l to about 10 g/l, preferably from about 0.1 g/l to about 1.5 g/l and is most preferably about 1.0 g/l.

          The composition also includes a soluble compound containing zirconium and preferably, fluoride. Examples of suitable zirconium comprising materials include, but  
 20 are not limited to, zirconium ammonium fluoride, dihydrogen hexafluorozirconate, potassium hexafluorozirconate, zirconium sulfate, zirconium carbonate, zirconium nitrate, and zirconium phosphate. Dihydrogen hexafluorozirconate is the most preferred zirconium comprising compound. The concentration of the zirconium comprising compound in the composition should preferably range from about 0.01 g/l to about 2.0  
 25 g/l, most preferably from about 0.05 g/l to about 0.5 g/l.

          The inventors have determined that the pH of the treatment composition should preferably be maintained from about 2.0 to about 7.0, more preferably between 2.8 and 7.0. The inventors have discovered that the corrosion protection afforded while  
 30 operating outside of the foregoing range (2.0-7.0) is substantially inferior and that the stability of the aqueous solution of the treatment composition outside of the preferred range is less than desired.

The treating bath preferably comprises ammonium hydroxide as a neutralization agent for the concentrate and the treatment solution made from the concentrate. Ammonium hydroxide is necessary in order to adjust the pH of the liquid concentrate to an elevated pH so that the concentrate will not become unstable.

5

The inventors have also discovered that the build-up of aluminum in the treatment composition bath may increase the ability of the bath to produce excellent corrosion resistance as compared to a fresh bath. The inventors have achieved 1,000 hours of salt spray resistance on panels that have been processed in old treatment baths.

10

To that end, a soluble aluminum salt may be added to the treatment composition of the present invention. Soluble aluminum salts that are usable in the invention include aluminum ammonium chloride, aluminum ammonium sulfate, aluminum nitrate, aluminum potassium sulfate and aluminum sulfate. If used, the aluminum salt should generally be present in the bath at a concentration of between 5 and 500 parts per million (ppm) as aluminum, with a preferred concentration of between 10 and 200 ppm as aluminum.

15

Typically, parts to be treated with the composition of this invention are cleaned to remove soils and other surface contamination. Preferably the parts are then deoxidized in an acid solution, which is capable of removing surface oxides, and then rinsed. A suitable acid solution for wrought alloys is a 50% nitric acid solution, although other acid solutions may also be used. The parts are then contacted with the zirconium tungstate composition of this invention by either immersion or by spraying for a period ranging from about 30 seconds to about 10 minutes. The treatment composition is preferably maintained at temperatures ranging from about 55°F to about 180°F, most preferably from about 70°F to about 120°F. The parts are then dried and/or baked, prior to painting or other processing.

20

25

Optional ingredients may be added to the treatment composition, including surfactants, accelerators, dyes, organic polymers, buffering agents and pH adjusting agents.

30

This invention is further described by the following examples, which should be taken as illustrative only and not limiting in any regard.

**Example 1:**

- 5 Metal parts are first cleaned to remove surface contamination, by soaking the parts in an alkaline cleaning solution, at 170°F for 10-15 minutes. In this example, the alkaline cleaning solution used is MacDermid TS 40A, at a concentration of 6 oz/gal, although other alkaline cleaning solutions may also be used. Next, the parts are rinsed for a period of about 2 minutes. The parts are deoxidized in a 50% nitric acid solution at ambient temperature for a period of about 1 minute, and are then subjected to a second rinsing. The parts are subjected to a conversion coating of the present invention for a period of 2 to 10 minutes at a temperature ranging from room temperature to about 125°F. The parts are then rinsed for a final time and are dried and/or baked. Finally, the parts may be painted or otherwise processed. Table 1 provides several examples of working bath concentrations of solutions that are usable in the present invention.

**Table 1. Suitable Bath Concentrations of Solutions of the Invention**

Component	Formulation A	Formulation B	Formulation C
Tungstic acid, hexaammonium salt	3.0 g/l	2.5 g/l	3.5 g/l
Dihydrogen hexafluorozirconate	3.0 g/l	2.5 g/l	3.5 g/l
Water	Diluted to 1 liter	Diluted to 1 liter	Diluted to 1 liter

20

**Example 2:**

- 25 The effect of heat treating on neutral salt spray test results for panels treated in a five minute immersion of the compositions of example 1 was investigated by baking sample panels at various temperatures for 10 minute each and comparing the results to that of panels coated with a chromate conversion coating. The results are shown in Table 2.

**Table 2. Comparison of Effect of Heat-Treating on Neutral Salt Spray Results for Tungstate Zirconium Coatings and Chromate Coatings**

Temperature °C	Hours to Failure	
	Tungstate-Zirconium Coating	Chromate Coating
150	168 hours	< 24 hours
200	144 hours	< 24 hours
250	144 hours	< 24 hours
300	312 hours	< 24 hours
350	312 hours	< 24 hours

- 5 As is readily seen, the panels treated with the composition of the instant invention provide much greater corrosion protection than similar panels coated with a chromate conversion coating at elevated temperatures.

Example 3:

- 10 Panels treated with the zirconium and tungsten solution were tested side by side with panels treated with a chromate conversion coating conforming to MIL-C-81706 and MIL-C-5541. For comparison purposes, bare aluminum panels were included in the test. The treated (or bare aluminum) panels were sprayed with primer and/or paint or were powder coated. The treated (or bare aluminum) panels were then subjected to a 2 mm
- 15 cross-hatch/tape-pull test in accordance with ASTM D 3359-87 Method B, the standard test method for measuring adhesion with tape. As expected, the bare aluminum panels resulted in consistent adhesion failures. On the other hand, the zirconium tungstate coated panels provided adhesion promotion that equaled or exceeded that of the chromate coated panels.

20

Example 4:

- The zirconium tungstate coated panels of the present invention were next tested side by side with panels treated with panels treated with the MIL-C-81706/MIL-C-5541 chromate and, for comparison purposes, bare aluminum panels after the panels had been
- 25 heated or baked at elevated temperatures.

In this example, the treated (or bare aluminum) panels were heated to temperatures of 150°C, 200°C, 250°C, 300°C, and 350°C for a 20-minute time period

prior to painting. The treated (or bare aluminum) panels were spray painted with a primer, and then painted.

- 5 The panels were then subjected to a 2 mm cross-hatch/tape-pull test in accordance with ASTM D 3359-87 Method B. The results demonstrated that the adhesion promotion of the tungstate zirconium treated panels far exceeded that of the bare aluminum panels or the chromate coated panels.

1  
2  
3  
4  
5  
6  
7  
8  
9  
10  
11  
12  
13  
14  
15  
16  
17  
18  
19  
20  
21  
22  
23  
24  
25  
26  
27  
28  
29  
30  
31  
32  
33  
34  
35  
36  
37  
38  
39  
40  
41  
42  
43  
44  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60  
61  
62  
63  
64  
65  
66  
67  
68  
69  
70  
71  
72  
73  
74  
75  
76  
77  
78  
79  
80  
81  
82  
83  
84  
85  
86  
87  
88  
89  
90  
91  
92  
93  
94  
95  
96  
97  
98  
99  
100